

THE CHEMISTRY AND TRANSFORMATIONS OF MERCURY AND ARSENIC IN ANAEROBIC SEDIMENTS

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LONG TERM GOALS

Mercury and Arsenic are important pollutants released from a variety of sources (ships, buoy batteries, etc.) into harbors and coastal waters. Both these elements can have important ecological effects and bioaccumulation of mercury in fish is a concern for human health. We thus need to understand the factors that control the fate of arsenic and mercury in harbors and coastal waters. This project focuses on the transformations of arsenic and mercury in the anoxic sediments that are characteristic of such environs. More specifically, the long term goals of this project are to elucidate the chemical and biological mechanisms that control the precipitation and dissolution of arsenic and mercury in anaerobic coastal sediments and to quantify the consequences of these processes in determining the potential release of these toxic elements to the water column and their accumulation in marine organisms.

OBJECTIVES

The specific objectives of this project are to 1) document the microbial reduction of the relatively immobile arsenate to the more mobile arsenite in anaerobic sediments; 2) study the conditions for arsenate reduction and precipitation of arsenite as the arsenic trisulfide solid; 3) study the dissolution of mercuric sulfide under various conditions; 4) quantify the rates of oxidation and reduction of dissolved mercury; and 5) elucidate the chemical conditions that enhance the rate of microbial uptake and methylation of mercury in anaerobic sediments.

APPROACH

The arsenic part of the project is based chiefly on laboratory studies with bacteria collected in the field. By studying both isolated bacteria in pure cultures and natural consortia we seek to establish the importance of arsenate respiration (i.e. elucidate the conditions for its reduction to arsenite) and of arsenite precipitation in the environment and determine the factors that accelerate or inhibit these transformations.

Our mercury work (which has been put to a lower priority because of funding cuts) is also based chiefly on laboratory studies, both chemical and microbiological. The chemical studies have focused on the dissolution of cinnabar (solid mercuric sulfide the principal form of mercury in anaerobic sediments) to release ionic (Hg(II)) and elemental (Hg(0)) mercury, the reduction of

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Hg(II) to the volatile Hg(0), and the oxidation of Hg(0) to Hg(II). The microbial studies are designed to quantify the effect of medium chemistry on the rate of intracellular uptake of mercury by bacteria and on the rate of Hg(II) methylation.

WORK COMPLETED

Arsenic. We have isolated two bacterial strains -- MIT-13 (now *Geospirillum arsenophilus*), and OREX-4 (now *Desulfotomaculum aurpigmentum*) -- that grow by dissimilatory reduction of arsenate, As(V), and characterized both organisms in terms of their metabolic capabilities. We have also studied the conditions for microbial precipitation of arsenic trisulfides in cultures of OREX-4 and elucidated the reasons why it does not occur in other cultures.

Mercury. We have undertaken a systematic study of the kinetics of HgS dissolution examining the effects of such factors as pH, oxygen concentration, light and the presence of organic acids. The dissolved mercury, as Hg(II) or Hg(0), can be subsequently oxidized or reduced. We are in the process of quantifying the rates of each of these chemical reactions under conditions typical of natural sediments.

In natural waters, mercury is methylated chiefly by sulfate reducing bacteria that live in anoxic waters or sediments and respire by reducing sulfate to sulfide. We have been testing the hypothesis that the presence of polysulfides (formed by reaction of sulfide with elemental sulfur) might enhance the rate of bacterial methylation of mercury via the formation of mercury polysulfide complexes that would keep the mercury in solution and diffuse rapidly through bacterial membranes.

RESULTS

Arsenic. We have established that MIT-13 and OREX-4 have very different metabolic capabilities. One can reduce N(V) (nitrate) as well as As(V), while the other can grow on S(VI) (sulfate) as well as As(V). While MIT-13 is gram-negative, OREX-4 is gram-positive and, according to 16S ribosomal RNA sequencing, the two organisms are phylogenetically quite distant. In addition to reducing As(V), OREX-4 precipitates arsenite, As (III), as As₂S₃ in S-containing medium. This precipitation occurs, at least in part, intracellularly and under conditions where no chemical precipitation is observed.

Mercury. As expected we have found that light greatly enhances the dissolution of mercuric sulfide as does oxygen. The dissolution process is complicated by the reduction of Hg(II) (by sulfur or organic species) and rapid re-oxidation of Hg(0) (ultimately by O₂). The oxidation of Hg(0) in the presence of oxygen is accelerated by high chloride concentrations (as found in seawater) and by the presence of appropriate particles. We have demonstrated that, in anoxic waters, mercury polysulfide complexes indeed form and enhance the solubility of mercury in sulfide waters. We have also found that the addition of elemental mercury (in the form of polysulfides or particulate sulfur) to cultures of sulfate reducers enhances markedly their rate of

mercury methylation. This result is complicated, however, by the changing concentrations of sulfur species in the cultures and control experiments are under way.

IMPACT

These results have modified radically our understanding of the processes that control the fate of arsenic and mercury in coastal waters. First it appears that arsenate respiration is likely widespread among bacterial phyla and common in contaminated anoxic environs. Further, the microbial precipitation of arsenic trisulfide, puts into question the general assumption that reduction of As(V) to As(III) makes As more mobile in the environment. On the contrary, As₂S₃ precipitation may provide a permanent sink for As in anaerobic sediments.

For mercury, our finding that Hg(0) can be rapidly oxidized implies that in many aquatic systems where this process should effectively decrease the net rate of Hg(0) volatilization, we have likely overestimated the rate of mercury release into the atmosphere. Finally, if our results showing that the formation of polysulfides increases many fold the rate of Hg methylation are confirmed, they will constitute a breakthrough in our understanding of the mechanisms of Hg methylation in anaerobic sediments and of the factors that control it.

TRANSITIONS

Not applicable at this point, but our results on Hg(0) oxidation are of great importance regarding the fate of elemental mercury released from discarded Aids to Navigation.

RELATED PROJECTS

This ONR project benefits from two ongoing projects (funded by EPA and NSF) dealing with the microbiology and chemistry of arsenic and mercury.

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